SECTION 2
PROTOCOL FOR EVALUATING NATURAL ATTENUATION

The primary objective of the natural attenuation investigation is to determine whether natural processes will be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives. Further, natural attenuation should be evaluated to determine if it can meet all appropriate Federal and State remediation objectives for a given site. This requires that projections of the potential extent of the contaminant plume in time and space be made. These projections should be based on historic variations in contaminant concentration, and the current extent and concentrations of contaminants in the plume in conjunction with measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent of monitored natural attenuation to provide sufficient evidence to demonstrate that the mechanisms of natural attenuation will meet the remediation objectives appropriate for the site. This can be facilitated by using conservative parameters in solute fate and transport models and numerous sensitivity analyses in order to better evaluate plausible contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently confirms the natural reduction and removal of the dissolved contaminant plume.

Figure 2.1 outlines the steps involved in a natural attenuation demonstration and shows the important regulatory decision points for implementing natural attenuation. For example, a Superfund Feasibility Study is a two-step process that involves initial screening of potential remedial alternatives followed by more detailed evaluation of alternatives that pass the screening step. A similar process is followed in a RCRA Corrective Measures Study and for sites regulated by State remediation programs. The key steps for evaluating natural attenuation are outlined in Figure 2.1 and include:

1) Review available site data and develop a preliminary conceptual model. Determine if receptor pathways have already been completed. Respond as appropriate.
2) If sufficient existing data of appropriate quality exist, apply the screening process described in Section 2.2 to assess the potential for natural attenuation.
3) If preliminary site data suggest natural attenuation is potentially appropriate, perform additional site characterization to further evaluate natural attenuation. If all the recommended screening parameters listed in Section 2.2 have been collected and the screening processes suggest that natural attenuation is not appropriate based on the potential for natural attenuation, evaluate whether other processes can meet the cleanup objectives for the site (e.g., abiotic degradation or transformation, volatilization, or sorption) or select a remedial option other than MNA.
4) Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of natural attenuation.
5) Simulate, if necessary, natural attenuation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term.
6) Identify potential receptors and exposure points and conduct an exposure pathways analysis.
7) Evaluate the need for supplemental source control measures. Additional source control may allow MNA to be a viable remedial option or decrease the time needed for natural processes to attain remedial objectives.

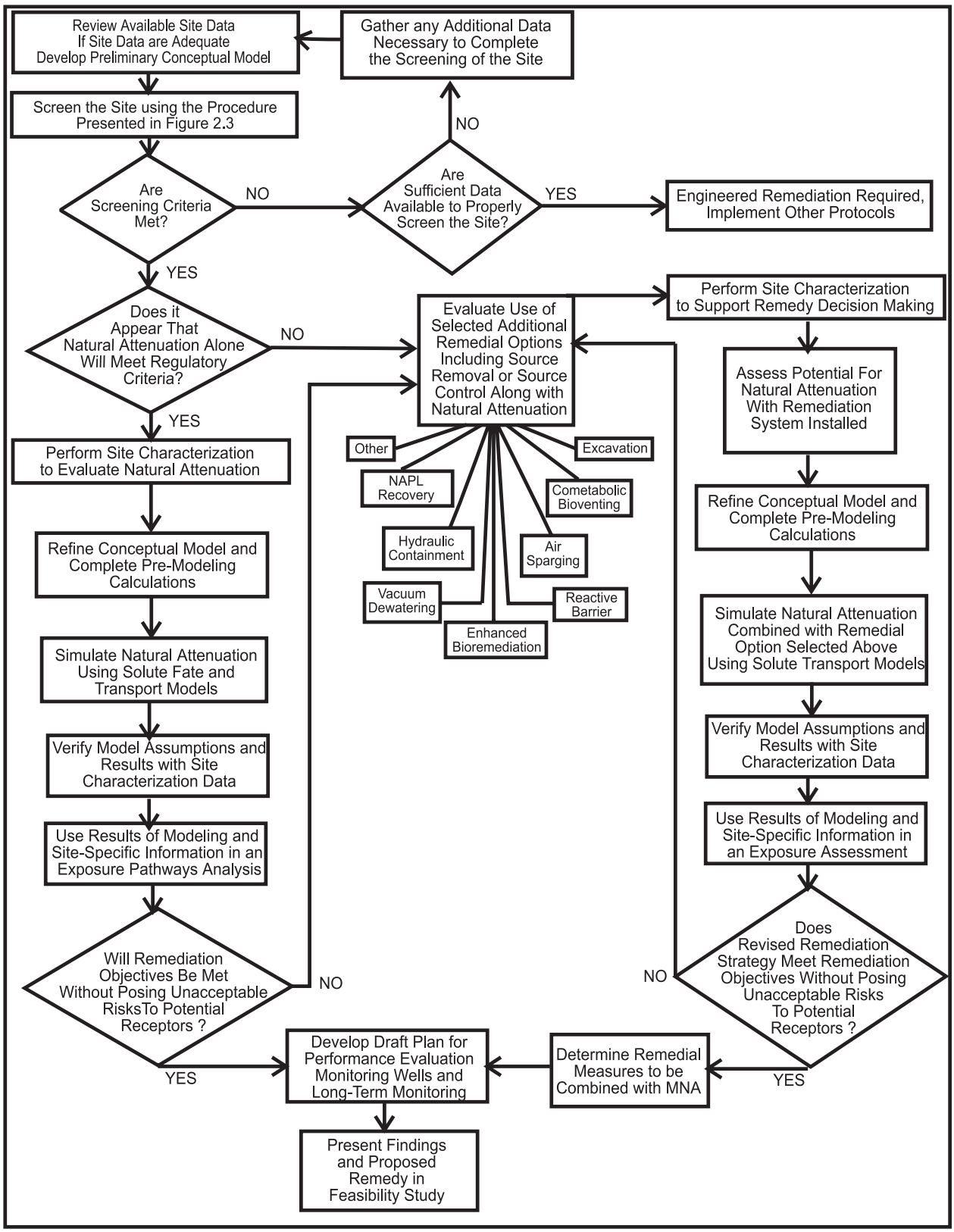

Figure 2.1 *Natural attenuation of chlorinated solvents flow chart.*

8) Prepare a long-term monitoring and verification plan for the selected alternative. In some cases, this includes monitored natural attenuation alone, or in other cases in concert with supplemental remediation systems.
9) Present findings of natural attenuation studies in an appropriate remedy selection document, such as a CERCLA Feasibility or RCRA Corrective Measures Study. The appropriate regulatory agencies should be consulted early in the remedy selection process to clarify the remedial objectives that are appropriate for the site and any other requirements that the remedy will be expected to meet. However, it should be noted that remedy requirements are not finalized until a decision is signed, such as a CERCLA Record of Decision or a RCRA Statement of Basis.

The following sections describe each of these steps in more detail.

2.1 REVIEW AVAILABLE SITE DATA AND DEVELOP PRELIMINARY CONCEPTUAL MODEL

The first step in the natural attenuation investigation is to review available site-specific data. Once this is done, it is possible to use the initial site screening processes presented in Section 2.2 to determine if natural attenuation is a viable remedial option. A thorough review of these data also allows development of a preliminary conceptual model. The preliminary conceptual model will help identify any shortcomings in the data and will facilitate placement of additional data collection points in the most scientifically advantageous and cost-effective manner possible.

The following site information should be obtained during the review of available data. Information that is not available for this initial review should be collected during subsequent site investigations when refining the site conceptual model, as described in Section 2.3.

- Nature, extent, and magnitude of contamination:
  - Nature and history of the contaminant release:
    --Catastrophic or gradual release of NAPL ?
    --More than one source area possible or present ?
    --Divergent or coalescing plumes ?
  - Three-dimensional distribution of dissolved contaminants and mobile and residual NAPLs. Often high concentrations of chlorinated solvents in ground water are the result of landfill leachates, rinse waters, or ruptures of water conveyance pipes. For LNAPLs the distribution of mobile and residual NAPL will be used to define the dissolved plume source area. For DNAPLs the distribution of the dissolved plume concentrations, in addition to any DNAPL will be used to define the plume source area.
  - Ground water and soil chemical data.
  - Historical water quality data showing variations in contaminant concentrations both vertically and horizontally.
  - Chemical and physical characteristics of the contaminants.
  - Potential for biodegradation of the contaminants.
  - Potential for natural attenuation to increase toxity and/or mobility of natural occurring metals.
- Geologic and hydrogeologic data in three dimensions (If these data are not available, they should be collected for the natural attenuation demonstration and for any other remedial investigation or feasibility study):
  - Lithology and stratigraphic relationships.
  - Grain-size distribution (gravels *vs*. sand *vs.* silt *vs.* clay).

  - Aquifer hydraulic conductivity (vertical and horizontal, effectiveness of aquitards, calculation of vertical gradients).
  - Ground-water flow gradients and potentiometric or water table surface maps (over several seasons, if possible).
  - Preferential flow paths.
  - Interactions between ground water and surface water and rates of infiltration/recharge.
- Locations of potential receptor exposure points:
  - Ground water production and supply wells, and areas that can be deemed a potential source of drinking water.
  - Downgradient and crossgradient discharge points including any discharges to surface waters or other ecosystems.
  - Vapor discharge to basements and other confined spaces.

In some cases, site-specific data are limited. If this is the case, all future site characterization activities should include collecting the data necessary to screen the site for the use of monitored natural attenuation as a potential site remedy. Much of the data required to evaluate natural attenuation can be used to design and evaluate other remedial measures.

Available site characterization data should be used to develop a conceptual model for the site. This conceptual model is a three-dimensional representation of the source area as a NAPL or region of highly contaminated ground water, of the surrounding uncontaminated area, of ground water flow properties, and of the solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data for the site. Data on the contaminant levels and aquifer characteristics should be obtained from wells and boreholes which will provide a clear three-dimensional picture of the hydrologic and geochemical characteristics of the site. High concentrations of dissolved contaminants can be the result of leachates, rinse waters and rupture of water conveyance lines, and are not necessarily associated with NAPLs.

This type of conceptual model differs from the conceptual site models commonly used by risk assessors that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. However, the conceptual model of the ground water system facilitates identification of these risk-assessment elements for the exposure pathways analysis. After development, the conceptual model can be used to help determine optimal placement of additional data collection points, as necessary, to aid in the natural attenuation investigation and to develop the solute fate and transport model. Contracting and management controls must be flexible enough to allow for the potential for revisions to the conceptual model and thus the data collection effort.

Successful conceptual model development involves:

- Definition of the problem to be solved (generally the three dimensional nature, magnitude, and extent of existing and future contamination).
- Identification of the core or cores of the plume in three dimensions. The core or cores contain the highest concentration of contaminants.
- Integration and presentation of available data, including:
  - Local geologic and topographic maps,
  - Geologic data,
  - Hydraulic data,
  - Biological data,
  - Geochemical data, and
  - Contaminant concentration and distribution data.

- Determination of additional data requirements, including:
  - Vertical profiling locations, boring locations and monitoring well spacing in three dimensions,
  - A sampling and analysis plan (SAP), and
  - Any data requirements listed in Section 2.1 that have not been adequately addressed.

Table 2.1 contains the recommended soil and ground water analytical methods for evaluating the potential for natural attenuation of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons. Any plan to collect additional ground water and soil quality data should include the analytes listed in this table. Table 2.2 lists the availability of these analyses and the recommended data quality requirements. Since required procedures for field sampling, analytical methods and data quality objectives vary somewhat among regulatory programs, the methods to be used at a particular site should be developed in collaboration with the appropriate regulatory agencies. There are many documents which may aid in developing data quality objectives (e.g.,U.S. EPA Order 5360.1 and U.S. EPA QA/G-4 Guidance for the Data Quality Objectives Process).

2.2 INITIAL SITE SCREENING

After reviewing available site data and developing a preliminary conceptual model, an assessment of the potential for natural attenuation must be made. As stated previously, existing data can be useful to determine if natural attenuation is capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives. This is achieved by first determining whether the plume is currently stable or migrating and the future extent of the plume based on (1) contaminant properties, including volatility, sorptive properties, and biodegradability; (2) aquifer properties, including hydraulic gradient, hydraulic conductivity, porosity and concentrations of native organic material in the sediment (TOC), and (3) the location of the plume and contaminant source relative to potential receptor exposure points (i.e., the distance between the leading edge of the plume and the potential receptor exposure points). These parameters (estimated or actual) are used in this section to make a preliminary assessment of the effectiveness of natural attenuation in reducing contaminant concentrations.

If, after completing the steps outlined in this section, it appears that natural attenuation will be a significant factor in contaminant removal and a viable remedial alternative, detailed site characterization activities that will allow evaluation of this remedial option should be performed. If exposure pathways have already been completed and contaminant concentrations exceed protective levels, or if such completion is likely, an engineered remedy is needed to prevent such exposures and should be implemented as an early action. For this case, MNA may still be appropriate to attain long-term remediation objectives for the site. Even so, the collection of data to evaluate natural attenuation can be integrated into a comprehensive remedial strategy and may help reduce the cost and duration of engineered remedial measures such as intensive source removal operations or pump-and-treat technologies.

2.2.1 Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation

Because biodegradation is usually the most important destructive process acting to reduce contaminant concentrations in ground water, an accurate estimate of the potential for natural biodegradation is important to consider when determining whether ground water contamination presents a substantial threat to human health and the environment. This information also will be useful when selecting the remedial alternative that will be most cost effective at eliminating or abating these threats should natural attenuation alone not prove to be sufficient.

Table 2.1 Soil, Soil Gas, and Ground-water Analytical Methods to Evaluate the Potential for Natural Attenuation of Chlorinated Solvents or Fuel Hydrocarbons in Ground Water. Analyses other than those listed in this table may be required for regulatory compliance.

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Soil	Aromatic and Chlorinated hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX]; Chlorinated Compounds	SW8260A		Data are used to determine the extent of soil contamination, the contamination mass present, and the potential for source removal.	Each soil sampling round	Sample volume approximately 100 ml; subsample and extract in the field using methanol or appropriate solvent; cool to 4°C.	Fixed-base
Soil	Biologically Available Iron (III)	Under development	HCI extraction followed by quantification of released iron (III)	Optional method that should be used when fuel hydrocarbons or vinyl chloride are present in the ground water to predict the possible extent of removal of fuel hydrocarbons and vinyl chloride via iron reduction.	One round of sampling in five borings, five cores from each boring	Minimum 1 inch diameter core samples collected into plastic liner. Cap and prevent aeration.	Laboratory
Soil	Total organic carbon (TOC)	SW9060 modified for soil samples	Procedure must be accurate over the range of 0.1 to 5 percent TOC	The rate of migration of petroleum contaminants in ground water is dependent upon the amount of TOC in the aquifer matrix.	At initial sampling	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C.	Fixed-base
Soil Gas	Fuel and Chlorinated VOCs	EPA Method TO-14		Useful for determining chlorinated and BTEX compounds in soil	At initial sampling	1-liter Summa Canister	Fixed-base
Soil Gas	Methane, Oxygen, Carbon dioxide	Field Soil Gas Analyzer		Useful for determining bioactivity in vadose zone.	At initial sampling and respiration testing	3-liters in a Tedlar bag, bags are reusable for analysis of methane, oxygen, or carbon dioxide.	Field

Table 2.1 (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Alkalinity	Hach Alkalinity test kit model AL AP MG-L	Phenolphthalein method	General water quality parameter used (1) as a marker to verify that all site samples are obtained from the same ground-water system and (2) to measure the buffering capacity of ground water.	Each sampling round	Collect 100 mL of water in glass container.	Field
Water	Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds)	SW8260A	Analysis may be extended to higher molecular weight alkyl benzenes	Method of analysis for BTEX and chlorinated solvents/byproducts, which are the primary target analytes for monitoring natural attenuation; method can be extended to higher molecular weight alkyl benzenes; trimethylben-zenes are used to monitor plume dilution if degradation is primarily anaerobic.	Each sampling round	Collect water samples in a 40 mL VOA vial; cool to 4°C; add hydrochloric acid to pH 2.	Fixed-base
Water	Arsenic	EPA 200.7 or EPA 200.9		To determine if anaerobic biological activity is solubilizing arsenic from the aquifer matrix material.	One round of sampling	Collect 100 ml in a glass or plastic container that is rinsed in the field with the ground water to be sampled. Unfiltered samples obtained using low flow sampling methods are preferred for analysis of dissolved metals. Adjust pH to 2 with nitric acid. Do not insert pH paper or an electrode into the sample.	Laboratory
Water	Chloride (optional, see data use)	Hach Chloride test kit model 8-P	Silver nitrate titration	As above, and to guide selection of additional data points in real time while in the field.	Each sampling round	Collect 100 mL of water in a glass container.	Field

Table 2.1 (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Chloride	Mercuric nitrate titration A4500-Cl^- C	Ion chromatography (IC) method E300 or method SW9050 may also be used	General water quality parameter used as a marker to verify that site samples are obtained from the same ground-water system. Final product of chlorinated solvent reduction.	Each sampling round	Collect 250 mL of water in a glass container.	Fixed-base
Water	Chloride (optional, see data use)	Hach Chloride test kit model 8-P	Silver nitrate titration	As above, and to guide selection of additional data points in real time while in the field.	Each sampling round	Collect 100 mL of water in a glass container.	Field
Water	Conductivity	E120.1/SW9050, direct reading meter		General water quality parameter used as a marker to verify that site samples are obtained from the same ground-water system.	Each sampling round	Collect 100 to 250 mL of water in a glass or plastic container.	Field
Water	Iron (II) (Fe^{+2})	Colorimetric Hach Method # 8146	Filter if turbid.	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese.	Each sampling round	Collect from a flow-through or over-flow cell / analyze at the well head.	Field
Water	Hydrogen (H_2)	Equilibration with gas in the field. Determined with a reducing gas detector.	Optional specialized analysis	Determined terminal electron accepting process. Predicts the possiblity for reductive dechlorination.	One round of sampling on selected wells.	Sampled at well head requires the production of 300 mL per minute of water for 30 minutes.	Field
Water	Manganese	EPA 200.7 or EPA 200.9		To determine if anaerobic biological activity is solubilizing manganese from the aquifer matrix material.	One round of sampling	Collect 100 ml in a glass or plastic container that is rinsed in the field with the ground water to be sampled. Unfiltered samples obtained using low flow sampling methods are preferred for analysis of dissolved metals. Adjust pH to 2 with nitric acid. Do not insert pH paper or an electrode into the sample.	Laboratory

Table 2.1 (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Methane, ethane, and ethene	Kampbell *et al.*, 1989 and 1998 or SW3810 Modified	Method published by researchers at the U.S. Environmental Protection Agency. Limited to few commercial labs.	The presence of CH_4 suggests BTEX degradation via methanogenesis. Ethane and ethene data are used where chlorinated solvents are suspected of undergoing biological transformation.	Each sampling round	Collect water samples in 50 mL glass serum bottles with gray butyl /Teflon-faced septa and crimp caps; add H_2SO_4 to pH less than 2, cool to 4°C.	Fixed-base
Water	Nitrate	IC method E300		Substrate for microbial respiration if oxygen is depleted.	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; add H_2SO_4 to pH less than 2, cool to 4°C.	Fixed-base
Water	Oxidation-reduction potential	A2580B	Measurements made with electrodes; results are displayed on a meter; protect samples from exposure to oxygen. Report results against a silver/silver chloride reference electrode. (Eh) is calculated by adding a correction factor specific to the electrode used.	The ORP of ground water influences and is influenced by the nature of the biologically mediated degradation of contaminants; the ORP (expressed as Eh) of ground water may range from more than 800 mV to less than -400 mV.	Each sampling round	Measure in a flow through cell or an over-flowing container filled from the bottom to prevent exposure of the ground water to the atmosphere.	Field
Water	Oxygen	Dissolved oxygen meter calibrated between each well according to the supplier's specifications	Refer to method A4500 for a comparable laboratory procedure.	The oxygen concentration is a data input to the Bioplume model; concentrations less than 1 mg/L generally indicate an anaerobic pathway.	Each sampling round	Measure dissolved oxygen on site using a flow-through cell or over-flow cell.	Field
Water	pH	Field probe with direct reading meter calibrated in the field according to the supplier's specifications.	Field	Aerobic and anaerobic biological processes are pH-sensitive.	Each sampling round	Measure dissolved oxygen on site using a flow-through cell or over-flow cell.	Field

Table 2.1 (Continued)

Matrix	Analysis	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Water	Sulfate (SO_4^{-2})	IC method E300	If this method is used for sulfate analysis, do not use the field method.	Substrate for anaerobic microbial respiration.	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C.	Fixed-base
Water	Sulfate (SO_4^{-2})	Hach method # 8051	Colorimetric, if this method is used for sulfate analysis, do not use the fixed-base laboratory method.	Same as above.	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C.	Field
Water	Temperature	Field probe with direct reading meter.	Field only	To determine if a well is adequately purged for sampling.	Each sampling round	Read from oxygen meter.	Field
Water	Total Organic Carbon also called DOC	SW9060	Laboratory	Used to classify plume and to determine if reductive dechlorination is possible in the absence of anthropogenic carbon.	Each sampling round	Measure using a flow-through cell or over-flow cell.	Laboratory

NOTES:

1. "Hach" refers to the Hach Company catalog, 1990.
2. "A" refers to *Standard Methods for the Examination of Water and Wastewater*, 18th edition, 1992.
3. "E" refers to *Methods for Chemical Analysis of Water and Wastes*, U.S. EPA, 1983.
4. "SW" refers to the *Test Methods for Evaluating Solid Waste, Physical, and Chemical Methods*, SW-846, U.S. EPA, 3rd edition, 1986.

Table 2.2 Objectives for Sensitivity and Precision to Implement the Natural Attenuation Protocol. Analyses other than those listed in this table may be required for regulatory compliance.

Matrix	Analysis	Method/Reference	Minimum Limit of Quantification	Precision	Availability	Potential Data Quality Problems
Soil	Aromatic and chlorinated hydrocarbons (benzene, toluene, ethylbenzene, and xylene [BTEX]; chlorinated compounds)	SW8260A	1 mg/Kg	Coefficient of Variation of 20 percent.	Common laboratory analysis.	Volatiles lost during shipment to laboratory; prefer extraction in the field.
Soil	Biologically Available Iron (III)	Under development	50 mg/Kg	Coefficient of Variation of 40 percent.	Specialized laboratory analysis.	Sample must not be allowed to oxidize.
Soil	Total organic carbon (TOC)	SW9060 modified for soil samples	0.1 percent	Coefficient of Variation of 20 percent.	Common laboratory analysis.	Samples must be collected from contaminant-transporting (i.e., transmissive) intervals.
Soil Gas	Fuel and Chlorinated VOCs	EPA Method TO-14	1 ppm (volume/volume)	Coefficient of Variation of 20 percent.	Common laboratory analysis.	Potential for atmospheric dilution during sampling.
Soil Gas	Methane, O_2, CO_2	Field Soil Gas Analyzer	1 percent (volume/volume)	Coefficient of Variation of 20 percent.	Readily available field instrument.	Instrument must be properly calibrated.
Water	Alkalinity	Hach alkalinity test kit model AL AP MG-L	50 mg/L	Standard deviation of 20 mg/L.	Common field analysis.	Analyze sample within 1 hour of collection.
Water	Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds)	SW8260A	MCLs	Coefficient of Variation of 10 percent.	Common laboratory analysis.	Volatilization during shipment and biodegradation due to improper preservation.
Water	Chloride	IC method E300	1 mg/L	Coefficient of Variation of 20 percent.	Common laboratory analysis.	----
Water	Chloride (optional, see data use)	Hach Chloride test kit model 8-P	1 mg/L	Coefficient of Variation of 20 percent.	Common field analysis.	Possible interference from turbidity.
Water	Conductivity	E120.1/SW9050, direct reading meter	50 $\mu S/cm^2$	Standard deviation of 50 $\mu S/cm^2$.	Common field probe.	Improperly calibrated instrument.

Table 2.2 (Continued)

Matrix	Analysis	Method/Reference	Minimum Limit of Quantification	Precision	Availability	Potential Data Quality Problems
Water	Hydrogen (H_2)[a/]	See Appendix A	0.1 nM	Standard deviation of 0.1nM.	Specialized field analysis.	Numerous, see Appendix A.
Water	Iron (II) (Fe^{2+}) XX	Colorimetric Hach Method # 8146	0.5 mg/L	Coefficient of Variation of 20 percent.	Common field analysis.	Possible interference from turbidity (must filter if turbid). Keep out of sunlight and analyze within minutes of collection.
Water	Major Cations	SW6010	1 mg/L	Coefficient of Variation of 20 percent.	Common laboratory analysis.	Possible colloidal interferences.
Water	Methane, ethane, and ethene	Kampbell *et al.*, 1989 or SW3810 Modified	1 µg/L	Coefficient of Variation of 20 percent.	Specialized laboratory analysis.	Sample must be preserved against biodegradation and collected without headspace (to minimize volatilization).
Water	Nitrate	IC method E300	0.1 mg/L	Standard deviation of 0.1 mg/L	Common laboratory analysis.	Must be preserved.
Water	Oxidation-reduction potential (ORP)	A2580B	plus or minus 300 mV	plus or minus 50 mV.	Common field probe.	Improperly calibrated electrodes or introduction of atmospheric oxygen during sampling.
Water	Oxygen	Dissolved oxygen meter	0.2 mg/L	Standard deviation of 0.2 mg/L.	Common field instrument.	Improperly calibrated electrodes or bubbles behind the membrane or a fouled membrane or introduction of atmospheric oxygen during sampling.
Water	Sulfate (SO_4^{2-})	IC method E300	5 mg/L	Coefficient of Variation of 20 percent.	Common laboratory.	Fixed-base.
Water	Sulfate (SO_4^{2-}) XX	Hach method # 8051	5 mg/L	Coefficient of Variation of 20 percent.	Common field analysis.	Possible interference from turbidity (must filter if turbid). Keep sample cool.
Water	pH	Field probe with direct reading meter.	0.1 standard units	0.1 standard units.	Common field meter.	Improperly calibrated instrument; time sensitive.
Water	Temperature	Field probe with direct reading meter.	0 degrees Celsius	Standard deviation of 1 degrees Celsius.	Common field probe.	Improperly calibrated instrument; time sensitive.
Water	Total Organic Carbon	SW9060	0.1 mg/L	Coefficient of Variation of 20 percent.	Common laboratory analysis.	

Notes:

** *Filter if turbidity gives a response from the photometer before addition of the reagents that is as large or larger than the specified minimum quantification limit.*

Over the past two decades, numerous laboratory and field studies have demonstrated that subsurface microorganisms can degrade a variety of chlorinated solvents (e.g., Bouwer *et al*., 1981; Miller and Guengerich, 1982; Wilson and Wilson, 1985; Nelson *et al*., 1986; Bouwer and Wright, 1988; Lee, 1988; Little *et al*., 1988; Mayer *et al*., 1988; Arciero *et al*., 1989; Cline and Delfino, 1989; Freedman and Gossett, 1989; Folsom *et al*., 1990; Harker and Kim, 1990; Alvarez-Cohen and McCarty, 1991a, 1991b; DeStefano *et al*., 1991; Henry, 1991; McCarty *et al*., 1992; Hartmans and de Bont, 1992; McCarty and Semprini, 1994; Vogel, 1994). Whereas fuel hydrocarbons are biodegraded through use as a primary substrate (electron donor), chlorinated aliphatic hydrocarbons may undergo biodegradation under three different circumstances: intentional use as an electron acceptor; intentional use as an electron donor; or, through cometabolism where degradation of the chlorinated organic is fortuitous and there is no benefit to the microorganism. At a given site, one or all of these circumstances may pertain, although at many sites the use of chlorinated aliphatic hydrocarbons as electron acceptors appears to be most important under natural conditions. In this case, biodegradation of chlorinated aliphatic hydrocarbons will be an electron-donor-limited process. Conversely, biodegradation of fuel hydrocarbons is an electron-acceptor-limited process.

In an uncontaminated aquifer, native organic carbon is used as an electron donor, and dissolved oxygen (DO) is used first as the prime electron acceptor. Where anthropogenic carbon (e.g., as fuel hydrocarbons) is present, it also will be used as an electron donor. After the DO is consumed, anaerobic microorganisms typically use additional electron acceptors (as available) in the following order of preference: nitrate, ferric iron oxyhydroxide, sulfate, and finally carbon dioxide. Evaluation of the distribution of these electron acceptors can provide evidence of where and how chlorinated aliphatic hydrocarbon biodegradation is occurring. In addition, because chlorinated aliphatic hydrocarbons may be used as electron acceptors or electron donors (in competition with other acceptors or donors), isopleth maps showing the distribution of these compounds and their daughter products can provide evidence of the mechanisms of biodegradation working at a site. As with BTEX, the driving force behind oxidation-reduction reactions resulting in chlorinated aliphatic hydrocarbon degradation is electron transfer. Although thermodynamically favorable, most of the reactions involved in chlorinated aliphatic hydrocarbon reduction and oxidation do not proceed abiotically. Microorganisms are capable of carrying out the reactions, but they will facilitate only those oxidation-reduction reactions that have a net yield of energy.

2.2.1.1 Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation

The following sections describe the biodegradation of those compounds that are most prevalent and whose behavior is best understood.

2.2.1.1.1 Electron Acceptor Reactions (Reductive Dehalogenation)

The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination. During this process, the chlorinated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. Figure 2.2 illustrates the transformation of chlorinated ethenes via reductive dechlorination. In general, reductive dechlorination occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. During reductive dechlorination, all three isomers of DCE can theoretically be produced. However, Bouwer (1994) reports that under the influence of biodegradation, *cis*-1,2-DCE is a more common intermediate than *trans*-1,2-DCE, and that 1,1-DCE is the least prevalent of the three DCE isomers when they are present as daughter products. Reductive dechlorination of chlorinated solvent compounds is associated with